



# Activity and stability of NiCe@SiO<sub>2</sub> multi-yolk-shell nanotube catalyst for tri-reforming of methane

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## ABSTRACT

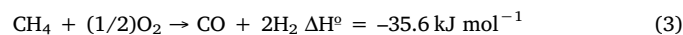
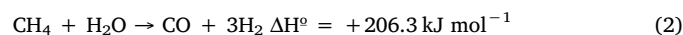
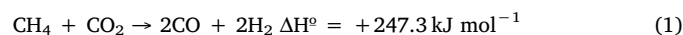
Tri-reforming of methane (TRM) produces syngas by directly utilizing flue gas from a fossil fuel-fired power plant without requiring post-combustion CO<sub>2</sub> separation. In this work, different yolk sizes of a NiCe@SiO<sub>2</sub> multi-yolk-shell nanotube catalyst were prepared and their catalytic properties were evaluated at different oxidizer (CO<sub>2</sub> + H<sub>2</sub>O + O<sub>2</sub>) to methane (O/M) feed ratios for TRM. The NiCe@SiO<sub>2</sub> multi-yolk-shell nanotube catalyst can exhibit longer stability than the conventional NiCe/SiO<sub>2</sub><sup>imp</sup> catalyst synthesized by impregnation method due to its controlled morphology and synergetic interactions of Ni–Ce and Ni–Si species. At a low O/M feed ratio of 1.0, NiCe@SiO<sub>2</sub> with smaller yolks (< 20 nm) shows higher resistance to carbon deposition than NiCe/SiO<sub>2</sub> with larger yolks due to the facile oxidation of carbon. On the other hand, NiCe@SiO<sub>2</sub> with larger yolks (> 30 nm) presents stable TRM activity at a high O/M feed ratio of 1.1, whereas NiCe@SiO<sub>2</sub> consisting of smaller yolks deactivates. Deactivation of NiCe@SiO<sub>2</sub> with smaller yolks can be explained by the re-oxidation of active Ni species, in which carbon formation and oxidation rates, and Ce<sup>3+</sup>/Ce<sup>4+</sup> redox properties play a crucial role. Our results indicate that the NiCe@SiO<sub>2</sub> multi-yolk-shell nanotube structures can provide high TRM activity, yet their structure should be tuned for stable performance by considering the yolk sizes and interaction of Ni–Ce species.

## 1. Introduction

CO<sub>2</sub> is the primary greenhouse gas, accounting for 82% of the United States (US) greenhouse gas emissions from human activities [1]. The combustion of fossil fuels for electricity generation remains the largest source of CO<sub>2</sub> emissions in the US [1–3]. CO<sub>2</sub> emissions are related to energy consumption and economic growth, and need to be controlled to mitigate their effect on climate change [4]. Many concepts have been explored to utilize CO<sub>2</sub> as a feedstock, including hydrogenation, reforming, mineralization, photoreduction, electroreduction, co-polymerization and bio-catalytic conversion [5–8]. Among them, syngas production through the application of reforming is proposed to be a valuable technology, which can be developed in the midterm by using novel catalytic routes to break C–O bonds and convert CO<sub>2</sub> to valuable chemicals [5,9,10].

Tri-reforming of methane (TRM) is a unique process that can be applied to utilize CO<sub>2</sub> emissions directly from a combustion source using natural gas as the primary reactant [11–14]. It has been reported

that fossil fuel-fired power plants integrated with the TRM process could reduce CO<sub>2</sub> emissions by up to 85% [15]. TRM involves synergetic combination of dry reforming of methane (DRM, (1)), steam reforming of methane (SRM, (2)), and partial oxidation of methane (POM, (3)) as shown in the following reactions:



In TRM, the CO<sub>2</sub> in the flue gas can be converted to syngas by DRM. DRM produces a H<sub>2</sub>/CO molar ratio of 1, which can potentially be used for the production of liquid hydrocarbons and oxygenates [16]. Although DRM has the advantage of utilizing CO<sub>2</sub> as an oxidizer, it is a highly endothermic reaction, needs a “pure” CO<sub>2</sub> stream and suffers from carbon deposition leading to catalyst deactivation [17–19]. Coupling DRM with SRM and POM can provide the advantage of adjusting the H<sub>2</sub>/CO molar ratios between 1 and 2.5, desired for the

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Fischer–Tropsch, methanol, and dimethyl ether synthesis [20–24]. Incorporation of  $\text{H}_2\text{O}$  and  $\text{O}_2$  as an oxidizer into the feed stream can eliminate carbon deposition and reduce energy needs through POM [25,26]. The synergistic combination of three reactions in TRM eliminates the need to pre-separate  $\text{CO}_2$ , which can further decrease the energy consumption and cost of operation.

Nickel-based catalysts are widely studied for TRM as they have a low cost compared to noble metals and have high activity at  $750^\circ\text{C}$  [11,12,14,27,28]. Nickel structures supported or promoted with  $\text{CeO}_2$  can improve the TRM activity, as  $\text{CeO}_2$  can store and release oxygen reversibly due to its oxygen vacancies and reversible valence redox property ( $\text{Ce}^{3+}/\text{Ce}^{4+}$ ) [29,30]. The addition of promoters to the Ni-based catalysts can further increase the activity and stability of the material by strengthening the metal–support interaction, providing high oxygen storage capacity and creating strong basic sites for  $\text{CO}_2$  activation [31–33]. In addition to the promoters, the effect of  $\text{CeO}_2$ -based supports on TRM activity has been investigated, in which small Ni particle sizes on  $\text{CeO}_2$ -based supports are reported to be beneficial for stable activity [34,35]. In these earlier studies, the effect of promoters or order of metal impregnation on the TRM activity has been examined. However, the interaction among active Ni, promoter, and support, and the effect of particle size on the TRM activity has not been identified.

Catalyst morphologies with unique physical and chemical properties, i.e., core/yolk–shell structures, have been investigated in reforming reactions and shown to have high resistance to carbon deposition and sintering due to the confinement effect and enhanced metal support interaction [36–45]. Compared to the core–shell, the yolk–shell structures (Scheme 1) can have a void space between the core metals and the outer shell materials that can provide additional properties to the material. The unique nanoreactor environment of the yolk–shell can facilitate chemical storage and confinement of the reactants, intermediates, and products. The cavity between the yolk and shell provides not only high exposed active areas but also a homogeneous environment for catalysis [46–50]. Few papers have been published on the core/yolk–shell catalysts for DRM and POM. These studies emphasize that shell thickness, yolk size, pore size and porosity can influence the activity and stability of core/yolk–shell catalysts for DRM [51–53]. In addition, core–shell catalysts promoted with La and Ce can further improve the stability of the catalyst by reducing the surface carbon growth in DRM and POM [46,54]. To date, there is only one study reported the activity of a  $\text{Ni@SiO}_2$  core–shell catalyst under various feed stream concentrations of TRM. In this study, formation of a core–shell structure is inconclusive and the effect of Ni particle size on the TRM activity at various oxidizer to methane feed ratios could not be understood [55].

It is important to note that TRM can be operated at different oxidizer ( $\text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$ ) to methane (O/M) feed ratios. Variations in methane concentration in the feed stream can dramatically influence

the catalyst performance for TRM. Generally, a catalyst for TRM should be able to exhibit high carbon resistance under reducing conditions ( $\text{O}/\text{M} \leq 1$ ), while re-oxidation of active metallic Ni to  $\text{Ni}^{2+}$  should be hindered under oxidizing conditions ( $\text{O}/\text{M} > 1$ ) [55,56]. Most of the studies involving core/yolk–shell structures were performed under DRM conditions. The effects of catalyst morphology and Ni–promoter interaction on the TRM activity at various O/M feed ratios have not been investigated. In this work, we have evaluated the TRM activity and stability of  $\text{NiCe@SiO}_2$  multi-yolk–shell nanotube catalysts at different O/M feed ratios, and identified the influence of yolk size and Ni–Ce interaction on the catalytic performance. To the best of our knowledge, this is the first study reporting the effect of morphology on the activity of the yolk–shell structured catalysts at various O/M feed ratios under TRM.

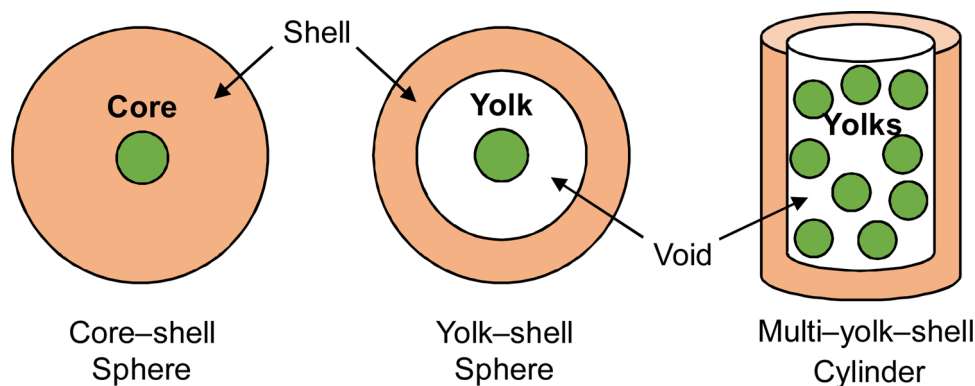
## 2. Experimental methods

### 2.1. Materials

The chemical reagents were used as purchased without any further purification: Nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%, Alfa Aesar) and cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99%, Sigma Aldrich) were used as the Ni and Ce yolk precursors. 1-hexadecyl trimethyl ammonium bromide (CTAB) ( $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$ , 98%, Alfa Aesar) was used as the surfactant and 1-butanol ( $\text{CH}_3(\text{CH}_2)_3\text{OH}$ , anhydrous, 99.8%, Sigma Aldrich) and cyclohexane ( $\text{C}_6\text{H}_{12}$ , 99%, Alfa Aesar) were used as the oil phase in the microemulsion solution. Hydrazine ( $\text{N}_2\text{H}_4$ , anhydrous, 98%, Sigma Aldrich) was used as a reducing agent and tetraethyl orthosilicate (TEOS) ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ , 99% Sigma Aldrich) was used as the silica shell precursor. Sodium hydroxide ( $\text{NaOH}$ , Fisher Chemical) and ammonium hydroxide solution ( $\text{NH}_4\text{OH}$ , 28%  $\text{NH}_3$ , Alfa Aesar) were used for base environmental conditions during the synthesis. Fumed silica ( $\text{SiO}_2$ , Sigma Aldrich) and Ethanol ( $\text{C}_2\text{H}_6\text{O}$ , anhydrous, Fisher Chemical) were used for synthesizing wet impregnated catalyst, and deionized (DI) water was used throughout the procedure. Methane (3.7 UHP, Praxair),  $\text{CO}_2$  (4.8 research, Praxair), air (ultra zero, Praxair), and  $\text{N}_2$  (100%, Airgas) were used for the tri-reforming of methane reaction.

### 2.2. Catalyst synthesis

The  $\text{NiCe@SiO}_2$  multi-yolk–shell nanotube catalyst was synthesized by reverse microemulsion method. The solution containing 0.2 M Ni ( $\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.05 M  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in 4 ml of DI water was added dropwise to the microemulsion dissolved in 0.17–0.26 M CTAB in 15 ml of 1-butanol and 80 ml of cyclohexane mixture. After stirring the solution for 1 h, the transparent microemulsion solution was heated up to  $70^\circ\text{C}$  in an oil bath, and 0.7 ml of hydrazine with 0.5 M NaOH in 1.5 ml DI was added to the solution dropwise, followed by further stirring for



Scheme 1. Schematic illustration of the core-shell, yolk-shell, and multi-yolk-shell nanotube structures.

40 min. The solution was cooled down to room temperature, and aged for another 2 h under stirring. Finally, 1.5 ml of TEOS was added to the solution dropwise, and after 1 h, 1.5 ml of ammonium hydroxide solution was added to the solution dropwise. The final solution was aged for 1 day for hydrolysis and condensation of the silica precursor. The solution was washed with ethanol and separated by centrifuging. The washed sample was dried at 100 °C overnight, and then calcined in static air at 500 °C for 4 h with a ramping rate of 5 °C min<sup>-1</sup>. Different yolk sizes and tube diameters can be obtained by controlling the water to surfactant (CTAB) molar ratio. A low water/CTAB ratio leads to larger yolk size with a shorter tube diameter, and a high water/CTAB ratio forms a smaller yolk size with a longer tube diameter. NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>B</sup>, and NiCe@SiO<sub>2</sub><sup>C</sup> catalysts were prepared in a water to CTAB ratio of 12.6, 15.8, and 18.9, respectively. For comparison, conventional NiCe/SiO<sub>2</sub><sup>Imp</sup> was synthesized by a wet impregnation method. 0.02 M Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.005 M Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and 0.5 g of silica were mixed in 50 ml ethanol. The whole mixture was stirred overnight, and the material was dried at 100 °C overnight, followed by calcination at 500 °C in stagnant air for 4 h with ramping temperature rate of 5 °C min<sup>-1</sup>.

### 2.3. Catalyst activity measurements

The performance of the catalyst for TRM was tested in a fixed-bed reactor at atmospheric pressure. 75 mg of the catalyst was placed between quartz wool in a quartz reactor with an inner diameter of 7 mm. Water was injected into an evaporator via a peristaltic pump and mixed with the reaction gases. The reaction gases (CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>) were introduced to the evaporator via mass flow controllers. The reactor was placed in a furnace and the temperature of the catalyst was measured by a K-type thermocouple placed inside the catalyst bed. The effluent gases were passed through a condenser in which water vapor was removed, and their concentration was measured with a gas chromatograph (GC) using a thermal conductivity detector (TCD). Prior to the reaction, all catalysts were reduced at 600 °C for 1 h with 25% H<sub>2</sub> balanced with N<sub>2</sub>. Following the reduction, the catalysts were heated up to a reaction temperature of 750 °C under N<sub>2</sub> flow. The TRM reaction was carried out for 20 h in a gas hourly space velocity (GHSV) of 60,000 ml g<sup>-1</sup> h<sup>-1</sup> at different O/M feed ratios including 0.85 (CH<sub>4</sub> : CO<sub>2</sub> : H<sub>2</sub>O : O<sub>2</sub> = 2.59 : 1 : 1 : 0.2), 1 (CH<sub>4</sub> : CO<sub>2</sub> : H<sub>2</sub>O : O<sub>2</sub> = 2.2 : 1 : 1 : 0.2), 1.1 (CH<sub>4</sub> : CO<sub>2</sub> : H<sub>2</sub>O : O<sub>2</sub> = 2 : 1 : 1 : 0.2) and 1.25 (CH<sub>4</sub> : CO<sub>2</sub> : H<sub>2</sub>O : O<sub>2</sub> = 1.76 : 1 : 1 : 0.2). The catalytic activity was calculated using the following equations:

$$\text{Conversion (\%)} = \frac{F_{\text{react,in}} - F_{\text{react,out}}}{F_{\text{react,in}}} \times 100 \quad (4)$$

$$\text{H}_2 \text{ yield (\%)} = \frac{F_{\text{H}_2,\text{out}}}{2F_{\text{CH}_4,\text{in}} + F_{\text{H}_2\text{O},\text{in}}} \times 100 \quad (5)$$

$$\text{CO yield (\%)} = \frac{F_{\text{CO},\text{out}}}{F_{\text{CO}_2,\text{in}} + F_{\text{CH}_4,\text{in}}} \times 100 \quad (6)$$

$$\text{H}_2/\text{CO ratio} = \frac{F_{\text{H}_2,\text{out}}}{F_{\text{CO},\text{out}}} \quad (7)$$

where F is the molar flow rate of the reagent species measured at the inlet and outlet of the reactor. The reproducibility of the catalytic activity for all experiments is within ± 5%.

### 2.4. Characterization

Field emission scanning electron microscopy (FESEM, Zeiss Ultra plus) and transmission electron microscopy (TEM, Hitachi H8000) images were obtained to investigate the morphology of the catalysts. Histogram distributions of yolk size was generated by analyzing TEM images, and 100 yolks were used for each distribution. The elemental

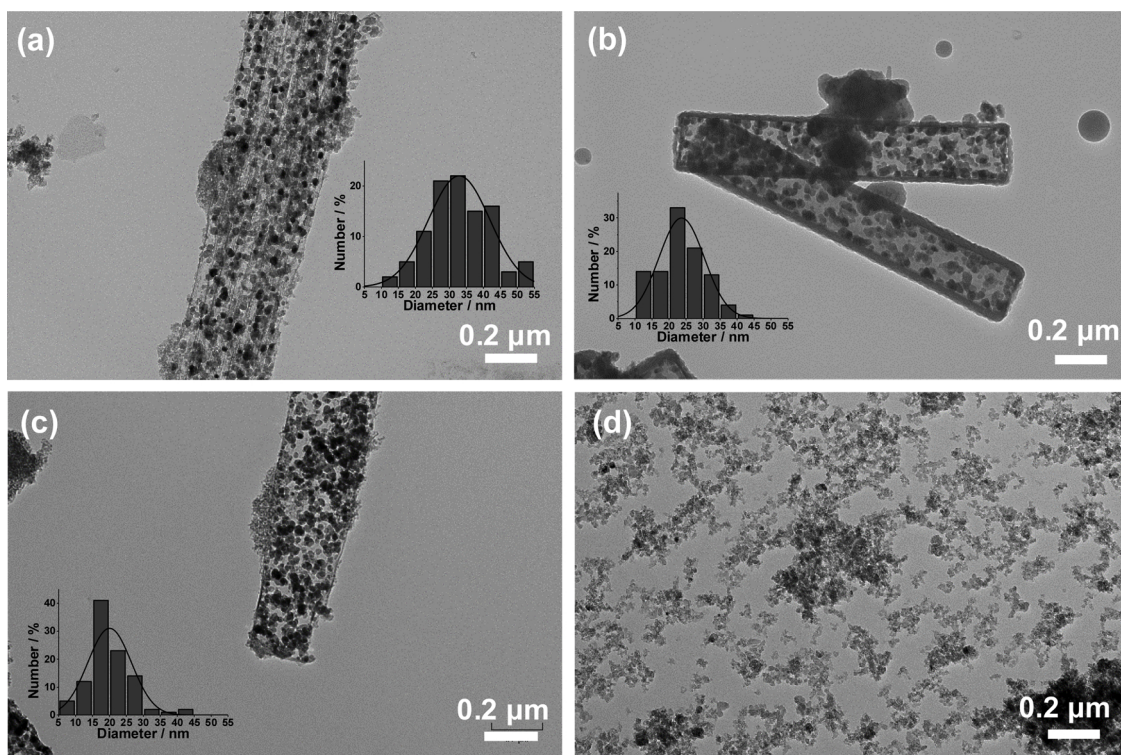
mapping of the catalysts was collected using a scanning transmission electron microscope (STEM, FEI Talos F200X). The weight percent of Ni and Ce in the samples was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES, Optima 2000 DV). Powder X-ray diffraction (XRD) patterns of the catalysts were obtained by using a Rigaku MiniFlex II with CuK<sub>α</sub> source radiation (α = 1.5406) for 2θ range of 10°–80° with a step rate of 2° min<sup>-1</sup>. The crystallite size of the components was calculated using Scherrer equation from the peaks at the (111) phase of each chemical element. The specific surface area of the sample was measured using a Micromeritics ASAP 2020. The samples were degassed at 300 °C for 7 h to remove the moisture prior to the measurements. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) was performed using a Micromeritics AutoChem II to identify the interaction between active species and supports and determine the reducibility of the catalysts. First, 50 mg of catalyst was heated up to 300 °C and held for 1 h under He flow to eliminate moisture and contaminations, and then cooled down to 30 °C. After the preparation step, the temperature of the catalyst was increased from 30 °C to 900 °C at a ramping rate of 10 °C min<sup>-1</sup> in a 10% H<sub>2</sub>/Ar mixture, and the H<sub>2</sub> consumption was monitored by TCD. The amount of H<sub>2</sub> reduced was calibrated by using CuO. H<sub>2</sub> pulse chemisorption experiments were performed with the same apparatus as H<sub>2</sub>-TPR to determine the dispersion of Ni particles. First, 100 mg of catalyst was reduced under 10% H<sub>2</sub>/Ar at 600 °C for 5 h. Then the catalyst was purged at 610 °C for 1 h and cooled down to 35 °C under He flow. H<sub>2</sub> pulse chemisorption was conducted at 35 °C in 10% H<sub>2</sub>/Ar with 8 min intervals. The oxidation states of the elements presented in catalysts were determined by X-ray photoelectron spectroscopy (XPS) with a Kratos Axis Ultra DLD using AlK<sub>α</sub> radiation, and the binding energy was calibrated to the signal of C 1s at 284.8 eV. The spectra were obtained after the samples were reduced in H<sub>2</sub>/Ar at 600 °C for 1 h. Thermogravimetric analysis (TGA) was employed using a TGA-50 Shimadzu to determine carbon deposition on the spent catalyst. The sample weight loss was characterized under air flow from 30 °C to 900 °C with a ramping temperature of 10 °C min<sup>-1</sup>. Raman spectra were obtained using an XploRA PLUS system from Horiba in the backscattering configuration at a 638 nm wavelength to determine the nature of carbon formed on the spent catalyst.

## 3. Results and discussion

### 3.1. Characterization of the fresh catalysts

Fig. 1 (a)–(c) show TEM images of NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>B</sup>, and NiCe@SiO<sub>2</sub><sup>C</sup> multi-yolk-shell nanotube catalysts synthesized in a solution containing water/CTAB molar ratios of 12.6, 15.8, and 18.9, respectively. The yolk nanoparticles of each catalyst are shown to be dispersed uniformly with a mean size of 32.9 nm, 23.7 nm, and 20.0 nm for NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>B</sup>, and NiCe@SiO<sub>2</sub><sup>C</sup>, respectively. The yolks of NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>B</sup>, and NiCe@SiO<sub>2</sub><sup>C</sup> are encapsulated by SiO<sub>2</sub> with an average tube diameter of 41.8 nm, 243.0 nm, and 275.0 nm, respectively. The multi-yolk-shell nanotube structure prepared at a high concentration of CTAB, i.e. NiCe@SiO<sub>2</sub><sup>A</sup>, consists of larger yolks with a smaller diameter tube, whereas the multi-yolk-shell nanotube structure synthesized at a low concentration of CTAB, i.e. NiCe@SiO<sub>2</sub><sup>C</sup>, has smaller yolks within a larger diameter tube. Compared to the multi-yolk-shell nanotube structured catalysts, conventional NiCe/SiO<sub>2</sub><sup>Imp</sup> synthesized by a wet impregnation method does not show any specific morphology (Fig. 1 (d)). It is important to note that Ce species are necessary to generate nanotube morphology. For instance, it is observed that Ni@SiO<sub>2</sub> without Ce forms a spherical yolk-shell structure rather than a nanotube structure when similar amount of Ni existed as in NiCe@SiO<sub>2</sub> (Fig. S1). This is because the nanotube formation and elongation is limited by the amount of gas released during the synthesis, in which Ce ions produce double amount of N<sub>2</sub> in comparison to Ni ions during reduction with hydrazine [57].





**Fig. 1.** TEM images of as-synthesized multi-yolk-shell nanotube catalysts synthesized in different water to CTAB ratios of (a) 12.6 (NiCe@SiO<sub>2</sub><sup>A</sup>), (b) 15.8 (NiCe@SiO<sub>2</sub><sup>B</sup>), (c) 18.9 (NiCe@SiO<sub>2</sub><sup>C</sup>) solution. The inset graph shows yolk size distribution. (d) TEM image of NiCe/SiO<sub>2</sub><sup>Imp</sup> synthesized by wet impregnation.

As shown in Fig. 2, the elemental mapping of STEM images of the NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>C</sup> catalysts confirm that the yolks are composed of Ni species surrounded by an outer shell consisting of only SiO<sub>2</sub>. As shown in Fig. 2 (a), accumulation of Ce on larger Ni yolks in NiCe@SiO<sub>2</sub><sup>A</sup> can be more pronounced than that in NiCe@SiO<sub>2</sub><sup>C</sup> with smaller yolks. Ce is found to be more dispersed throughout the catalysts, yet it is mostly accumulated on the Ni yolks indicating the possible Ni–Ce interaction. It is important to note that characteristic X-ray signals detected for Ce in the energy dispersive X-ray (EDX) spectra is low compared to Ni and Si. Although most of the Ce components are inside the nanotube structures, Ce pixels observed outside the nanotubes are possibly due to the low signal-to-noise ratio. The contrast change of Si between the edges and inner parts of the nanotube indicates that the SiO<sub>2</sub> shell has a cylindrical tube morphology with the presence of interstitial voids. Both the TEM and STEM images cannot definitively confirm whether the nanotubes are capped at each end. However, the overview SEM images of NiCe@SiO<sub>2</sub><sup>C</sup>, shown in Fig. S2, confirm that the tube structure is hollow in the inside, and both Ni and Ce particles are attached to the inner walls of the hollow tube.

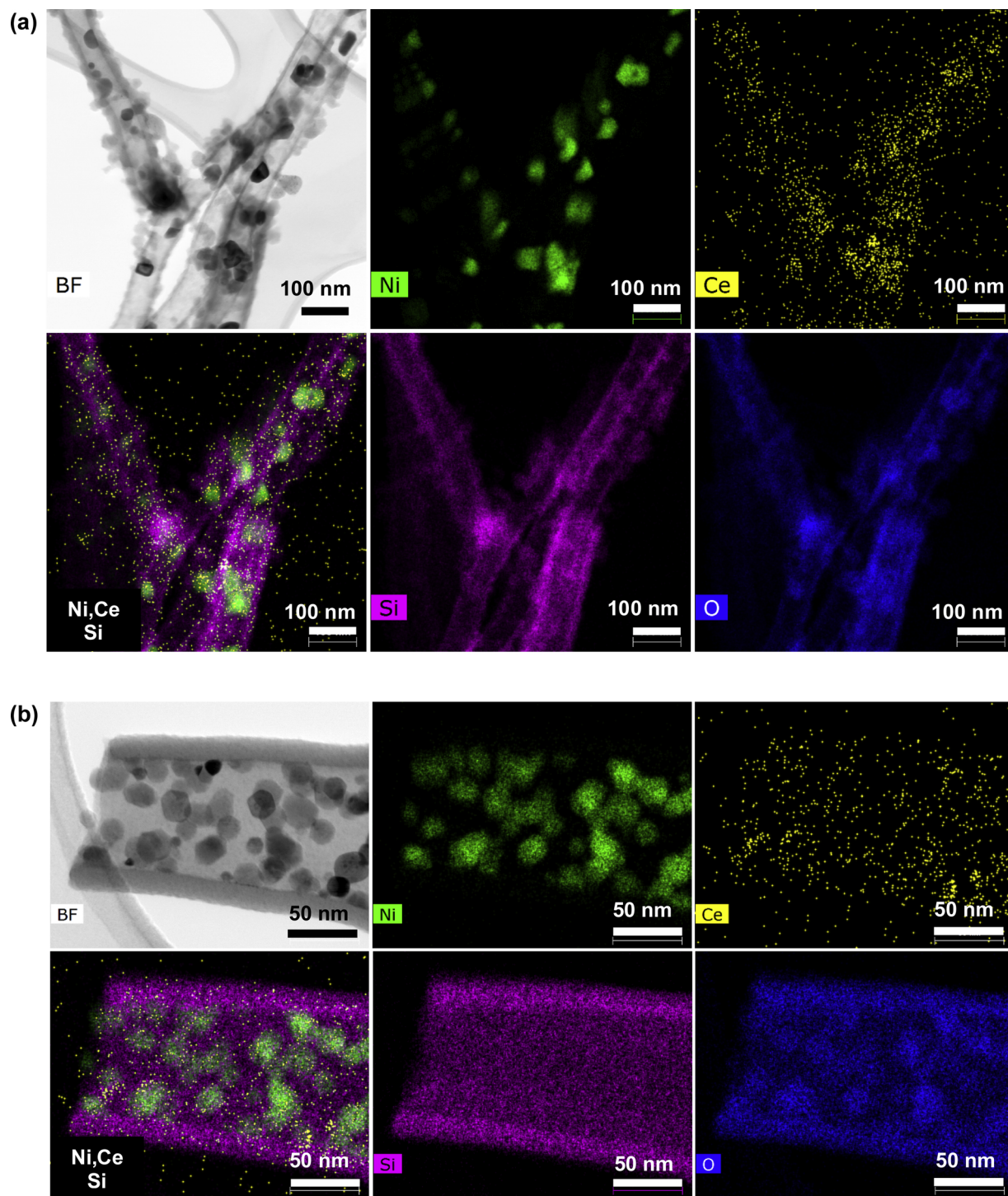
The XRD measurements of the as-synthesized NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup> are shown in Fig. 3. All three catalysts show NiO and CeO<sub>2</sub> diffraction patterns with an amorphous SiO<sub>2</sub> structure. The peaks at 2-theta of 37.66°, 43.69°, and 63.24° are identified as NiO, and the other peaks at 29.20°, 33.74°, 48.10°, 56.92°, and 75.74° belong to the cubic CeO<sub>2</sub> structure. The broad peak at 21.26° indicates the formation of amorphous SiO<sub>2</sub> shell. Based on the XRD patterns, the NiCe@SiO<sub>2</sub><sup>A</sup> catalyst shows the largest NiO crystallite size of 18.3 nm, followed by 16.2 nm for NiCe@SiO<sub>2</sub><sup>C</sup> and 14.3 nm for NiCe/SiO<sub>2</sub><sup>Imp</sup> (Table 1). The crystallite sizes of CeO<sub>2</sub> for the NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup> and NiCe/SiO<sub>2</sub><sup>Imp</sup> catalysts are found to be 6.7 nm, 8.5 nm, and 4.3 nm, respectively. NiCe/SiO<sub>2</sub><sup>Imp</sup> has the lowest CeO<sub>2</sub> crystallite size suggesting that ceria has higher dispersion and larger amount of oxygen vacancies than NiCe@SiO<sub>2</sub><sup>A</sup> followed by NiCe@SiO<sub>2</sub><sup>C</sup> [58]. The average yolk size of NiCe@SiO<sub>2</sub><sup>A</sup> measured by TEM (32.9 nm) is much larger than the NiO crystallite size calculated by XRD (18.3 nm) indicating

that the yolks in NiCe@SiO<sub>2</sub><sup>A</sup> are possibly formed with grain. On the other hand, the average yolk size of NiCe@SiO<sub>2</sub><sup>C</sup> by TEM (20.0 nm) matches reasonably well with the NiO crystallite size (16.2 nm). Fig. S3 represents the XRD patterns of NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup> after one hour of H<sub>2</sub> reduction at 600 °C. The peaks at 2-theta of 45.08°, 52.4°, and 76.84° correspond to metallic Ni phase. The NiO phase is not detected, which indicates that NiO was fully reduced to metallic Ni in all catalysts. The Ni crystallite size of NiCe/SiO<sub>2</sub><sup>Imp</sup> has the smallest value of 10.4 nm followed by 12.2 nm for NiCe@SiO<sub>2</sub><sup>A</sup> and 14.9 nm for NiCe@SiO<sub>2</sub><sup>C</sup>. The crystalline CeO<sub>2</sub> peaks get broader after the reduction, indicating that the phase transition of crystalline CeO<sub>2</sub> into Ce<sub>2</sub>O<sub>3</sub> has been initiated. For NiCe/SiO<sub>2</sub><sup>Imp</sup>, no CeO<sub>2</sub> peaks are observed due to the formation of highly dispersed CeO<sub>x</sub> particles [59].

The textural properties of the catalysts such as specific surface area and metal weight percentages are presented in Table 1. The NiCe@SiO<sub>2</sub><sup>A</sup> catalyst with smaller tube diameter provides larger surface area than the NiCe@SiO<sub>2</sub><sup>C</sup> catalyst, while the NiCe/SiO<sub>2</sub><sup>Imp</sup> catalyst has the highest surface area of 486.0 m<sup>2</sup> g<sup>−1</sup> among three catalysts. The weight percentages of Ni and Ce are measured to be in between 7.2–8.2 wt.% and 4.6–5.3 wt.% by ICP-OES in all three catalysts, respectively. The nitrogen adsorption-desorption isotherms of the NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup> catalysts are shown in Fig. S4. The isotherms of NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>C</sup> indicate type IV isotherm with H3 hysteresis, while NiCe/SiO<sub>2</sub><sup>Imp</sup> has a type IV isotherm with H2 hysteresis. Both H2 and H3 hysteresis indicate that all three catalysts have a porous structure. However, isotherms of type IV with H3 hysteresis can be found in a hierarchical porous structure consisting of mesopores and macropores, which is consistent with the morphology of the multi-yolk-shell nanotube structure [60].

H<sub>2</sub>-TPR experiments were conducted to determine the reducibility of the as-synthesized catalysts and interaction between the active sites and support. The H<sub>2</sub>-TPR profiles of the Ni@SiO<sub>2</sub>, Ni/SiO<sub>2</sub><sup>Imp</sup>, and Ce/SiO<sub>2</sub><sup>Imp</sup> catalysts were also analyzed to elucidate the effect of the Ce promoter (Fig. S5). As shown in Fig. 4, three temperature regions are found to exist for the NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup>





**Fig. 2.** STEM-EDX elemental mapping (Ni: green, Ce: yellow, Si: magenta, and O: blue) of (a) NiCe@SiO<sub>2</sub><sup>A</sup> and (b) NiCe@SiO<sub>2</sub><sup>C</sup> (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

catalysts. The first H<sub>2</sub> consumption peak of  $\alpha$  at temperatures between 215 °C and 400 °C is attributed to the combination of two reduction peaks of bulk NiO and aggregated NiO particles interacting more with the oxygen vacancies of CeO<sub>2</sub>, in which the latter is expected to be at lower temperatures as oxygen vacancies improve the reducibility of NiO [32,43,61]. Compared to Ni@SiO<sub>2</sub> (Fig. S5), the  $\alpha$  peak in the Ce promoted catalysts shifts to a lower temperature (311 °C) for NiCe@SiO<sub>2</sub><sup>A</sup> and a higher temperature (333 °C) for NiCe@SiO<sub>2</sub><sup>C</sup>. This can be explained by the yolk size effect and the formation of oxygen vacancies in the CeO<sub>2</sub> lattice, as smaller yolks have less Ni–Ce interaction and are

harder to be reduced than the catalyst with larger yolks [62]. The H<sub>2</sub> consumption peak of  $\beta$  in the medium temperature region is associated with the dispersed Ni species interacting with CeO<sub>2</sub> [63]. Formation of the  $\beta$  peak at slightly higher temperatures than the bulk NiO one has been observed by several other researchers [32,62]. It is possible that dispersed Ni particles might have stronger interaction with SiO<sub>2</sub> support, which can shift the Ni–Ce reduction peaks to a higher temperature than the bulk NiO one [46,62]. In the case of NiCe/SiO<sub>2</sub><sup>imp</sup>, the  $\alpha$  peak consists of NiO particles interacting more with the surface oxygen vacancies of CeO<sub>2</sub>, and the NiO reduction peak observed at 352 °C on Ni/

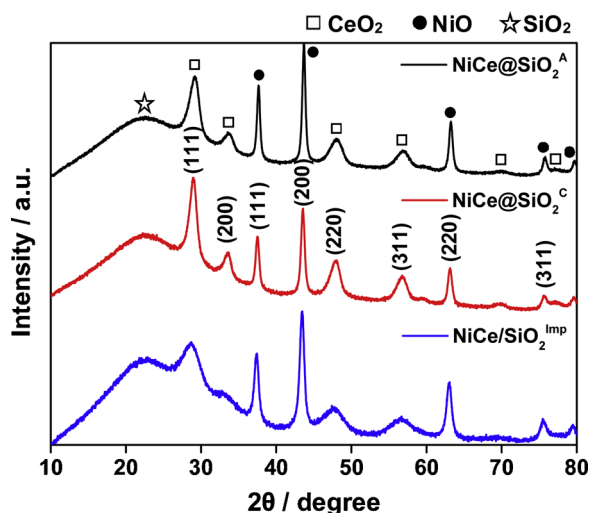


Fig. 3. XRD patterns of as-synthesized NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup>.

SiO<sub>2</sub><sup>Imp</sup> (Fig. S5) shifts to 386 °C after Ce promotion due to an enhanced NiO–SiO<sub>2</sub> interaction. The H<sub>2</sub> consumption peak of γ at temperatures above 400 °C is assigned to the NiO particles strongly bonded to the SiO<sub>2</sub> support. The broad γ peak for multi-yolk-shell nanotube catalysts is located in a higher temperature region compared to the impregnated catalyst. This indicates that NiO–SiO<sub>2</sub> interaction in NiCe@SiO<sub>2</sub> is stronger than that in NiCe/SiO<sub>2</sub><sup>Imp</sup> due to the encapsulation of Ni and Ce yolks by mesoporous SiO<sub>2</sub> [38,64]. The H<sub>2</sub> uptake of the multi-yolk-shell nanotube and impregnated catalysts are compared with the actual Ni amount loaded on the catalyst, as shown in Table 2. The overall H<sub>2</sub> consumption is much larger than the theoretical amount of Ni on all three catalysts due to the lattice oxygen reduction of CeO<sub>2</sub> by hydrogen spillover on Ni [32,63]. The H<sub>2</sub> uptake ratio of α/β for the NiCe@SiO<sub>2</sub> multi-yolk-shell nanotube catalyst is approximately 20 times higher than that of NiCe/SiO<sub>2</sub><sup>Imp</sup> indicating that most of H<sub>2</sub> is consumed by the bulk NiO and aggregated NiO particles interacting with CeO<sub>2</sub>. Compared to NiCe@SiO<sub>2</sub><sup>C</sup>, the higher overall H<sub>2</sub> consumption observed on NiCe@SiO<sub>2</sub><sup>A</sup> indicates that larger yolks are easily reduced due to the formation of more oxygen vacancies in the CeO<sub>2</sub> lattice.

The Ni particle size and dispersion estimated from the H<sub>2</sub> chemisorption measurements is presented in Table 3. For NiCe@SiO<sub>2</sub> multi-yolk-shell nanotube catalysts, Ni particle size is over 290 nm and much larger than the Ni size observed in TEM and XRD. The large particle size obtained for all catalysts from H<sub>2</sub> chemisorption does not represent the actual Ni particle size, indicating that Ni sites are not available to react with H<sub>2</sub>. This difference can be explained by the lack of Ni sites for H<sub>2</sub> chemisorption due to the strong Ni–Ce interaction and partially embedded Ni particles in the SiO<sub>2</sub> support [49,50,53]. The effect of latter on Ni particle size has more pronounced in the multi-yolk-shell catalysts compared to the impregnated catalyst, leading to a much larger Ni particle size. As shown in the H<sub>2</sub>-TPR experiments (Fig. 4), the γ reduction peak is located at a high temperature for the multi-yolk-shell nanotube catalysts indicating a strong NiO–SiO<sub>2</sub>

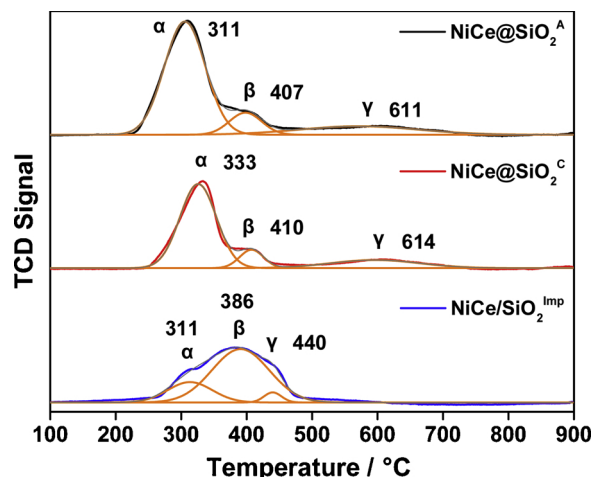


Fig. 4. H<sub>2</sub>-TPR profiles of NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup>.

Table 2

H<sub>2</sub> uptake during H<sub>2</sub>-TPR experiments with NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup>.

Catalysts	Overall Ni/mmol	H <sub>2</sub> uptake/mmol			α/β
		α	β	γ	
NiCe@SiO <sub>2</sub> <sup>A</sup>	0.070	0.084	0.013	0.019	6.5
NiCe@SiO <sub>2</sub> <sup>C</sup>	0.064	0.056	0.008	0.013	7.0
NiCe/SiO <sub>2</sub> <sup>Imp</sup>	0.053	0.017	0.055	0.003	0.3

Table 3

Physicochemical properties of NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup>.

Catalysts	Ni particle size <sup>a</sup> /nm	Ni dispersion <sup>a</sup> /%	Ce <sup>3+</sup> /(Ce <sup>3+</sup> + Ce <sup>4+</sup> ) <sup>b</sup> /%
NiCe@SiO <sub>2</sub> <sup>A</sup>	327.3	0.31	61.6
NiCe@SiO <sub>2</sub> <sup>C</sup>	292.4	0.35	36.1
NiCe/SiO <sub>2</sub> <sup>Imp</sup>	59.1	1.71	62.9

<sup>a</sup> Calculated based on H<sub>2</sub> chemisorption.

<sup>b</sup> Obtained from XPS deconvolution.

interaction. Ni dispersion has also been calculated through H<sub>2</sub> chemisorption measurements. As shown in Table 3, The NiCe/SiO<sub>2</sub><sup>Imp</sup> exhibits the highest Ni dispersion of 1.71%, followed by 0.35% and 0.31% for NiCe@SiO<sub>2</sub><sup>C</sup> and NiCe@SiO<sub>2</sub><sup>A</sup>, respectively. Ni dispersions have previously been reported in the range of 0.12–0.27% for Ni based core/yolk-shell structures, which are in consistent with our work [53,65]. The higher Ni dispersion observed on NiCe/SiO<sub>2</sub><sup>Imp</sup> compared to the multi-yolk-shell nanotube catalysts is consistent with the smaller Ni particle size and higher surface area measured on the NiCe/SiO<sub>2</sub><sup>Imp</sup> catalyst. It is important to note that Ni dispersion on the core/yolk-shell structure in which the active metal is encapsulated by a support can be influenced by the shell material and strong metal-support interaction [53].

Analysis of the core level XPS spectra of Ni and Ce species shows consistent results with the H<sub>2</sub>-TPR measurement. As shown in Fig. 5 (a),

Table 1

Textural properties of NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup>.

Catalysts	NiO crystallite size <sup>a</sup> /nm	CeO <sub>2</sub> crystallite size <sup>a</sup> /nm	S <sub>BET</sub> /m <sup>2</sup> g <sup>-1</sup>	Ni loading/wt. %	Ce loading/wt. %
NiCe@SiO <sub>2</sub> <sup>A</sup>	18.3 ± 0.2	6.7 ± 1.3	400.3	8.2	5.2
NiCe@SiO <sub>2</sub> <sup>C</sup>	16.2 ± 0.8	8.5 ± 1.1	366.9	7.5	5.3
NiCe/SiO <sub>2</sub> <sup>Imp</sup>	14.3 ± 0.5	4.3 ± 0.3	486.0	7.2	4.6

<sup>a</sup> Crystallite size of NiO and CeO<sub>2</sub>, estimated according to the Scherrer equation applied to (111) phase.

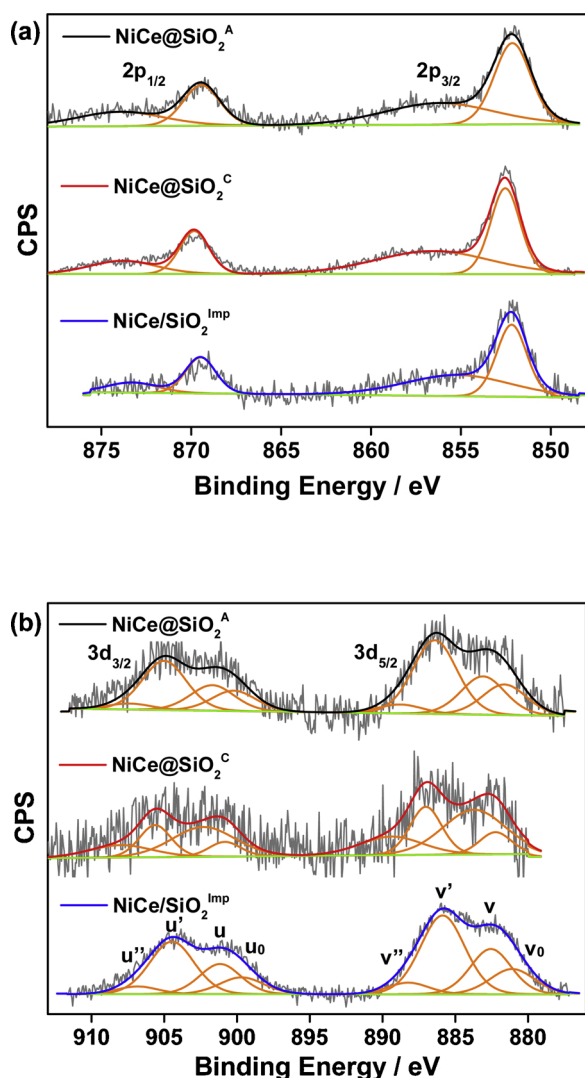


Fig. 5. (a) Ni 2p and (b) Ce 3d XPS spectra of reduced NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup>.

the Ni 2p core level spectra of the reduced NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup> catalysts have characteristic metallic Ni peaks of Ni 2p<sub>3/2</sub> (852.2 eV) and Ni 2p<sub>1/2</sub> (869.5 eV) accompanied by shake-up structures [35,46]. Fig. 5 (b) shows the Ce 3d core level XPS spectra of the reduced samples. The Ce core level spectra can be deconvoluted into multiple peaks for Ce 3d<sub>5/2</sub> (v) and Ce 3d<sub>3/2</sub> (u). The v and v' bands are attributed to Ce<sup>4+</sup>, whereas v<sub>0</sub> and v' bands are assigned to Ce<sup>3+</sup>. The other bands (v'' and u'') available for Ce could not be detected due to the low signal-to-noise ratio. The relative Ce<sup>3+</sup> concentration on the catalyst is calculated by the ratio of integrated Ce<sup>3+</sup> peaks to the total Ce<sup>3+</sup> and Ce<sup>4+</sup> peaks (Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>)). It has been found that NiCe/SiO<sub>2</sub><sup>Imp</sup> has the highest Ce<sup>3+</sup> concentration of 62.9% followed by 61.6% and 36.1% for NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>C</sup>, respectively (Table 3). This shows that more oxygen vacancies formed in the CeO<sub>2</sub> lattice by the dispersed NiO particles in NiCe/SiO<sub>2</sub><sup>Imp</sup> and aggregated NiO yolks in NiCe@SiO<sub>2</sub><sup>A</sup>.

### 3.2. TRM activity

The experiments for TRM were carried out at different O/M feed ratios to determine the activity and stability of the multi-yolk-shell nanotube and impregnated catalysts. Fig. 6 (a) and (b) illustrate CO<sub>2</sub> and CH<sub>4</sub> conversions at 750 °C at O/M feed ratios of 1.1 and 1.0, respectively. As shown in Fig. 6 (a), NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe/SiO<sub>2</sub><sup>Imp</sup> have

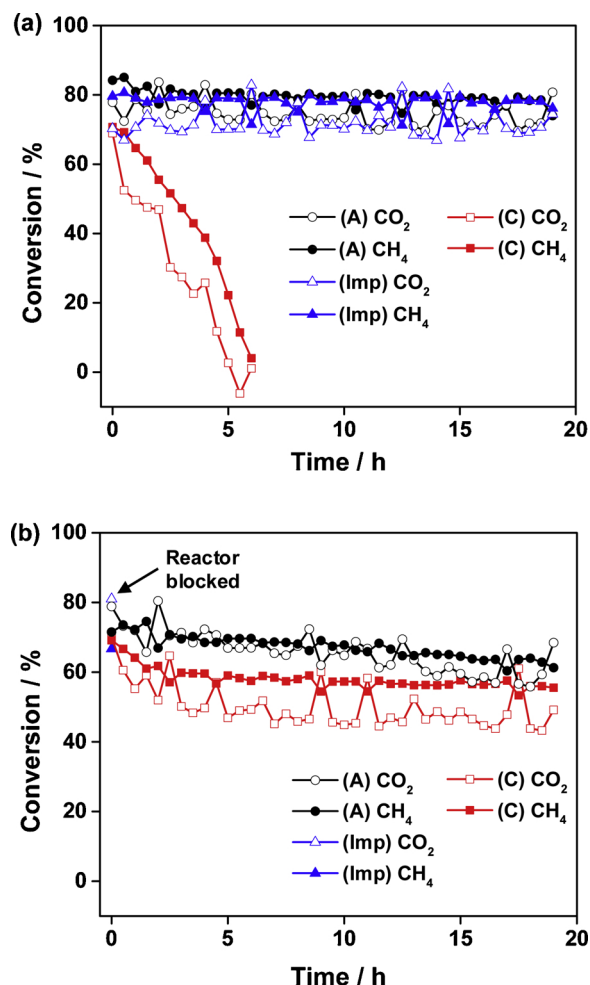


Fig. 6. CO<sub>2</sub> and CH<sub>4</sub> conversions of (A) NiCe@SiO<sub>2</sub><sup>A</sup>, (C) NiCe@SiO<sub>2</sub><sup>C</sup>, and (Imp) NiCe/SiO<sub>2</sub><sup>Imp</sup> catalysts at oxidizer to methane (O/M) ratios of (a) 1.1 and (b) 1.0 feed stream at 750 °C. The thermodynamic equilibrium conversions of CO<sub>2</sub> and CH<sub>4</sub> are 75.9% and 92.8% for O/M of 1.1 and 81.1% and 89.6% for O/M of 1.0, respectively.

comparable CO<sub>2</sub> conversions of 75% and 72%, and CH<sub>4</sub> conversions of 79% and 78% at O/M ratio of 1.1, respectively. NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe/SiO<sub>2</sub><sup>Imp</sup> present H<sub>2</sub> and CO yields of 75% and 77%, and 79% and 72% with the same H<sub>2</sub>/CO ratio of 1.7, respectively (Fig. S6). Both catalysts keep their activities stable over the 20 h period of reaction. In contrast, NiCe@SiO<sub>2</sub><sup>C</sup> shows an initial CO<sub>2</sub> and CH<sub>4</sub> conversions of 69% and 71%, respectively, yet both CO<sub>2</sub> and CH<sub>4</sub> conversions drop to below 5% within about 5 h. TRM activity of NiCe@SiO<sub>2</sub><sup>A</sup> with larger yolks was further tested at a higher O/M feed ratio of 1.25 to examine the catalytic activity and potential deactivation of the catalyst (Fig. S7). The result shows that the NiCe@SiO<sub>2</sub><sup>A</sup> catalyst still presents a stable activity with conversions of 67% and 84% for CO<sub>2</sub> and CH<sub>4</sub>, respectively. As the O/M feed ratio decreases to 1.0, the catalysts show distinctive behavior compared to those tested at the O/M feed ratio of 1.1. As shown in Fig. 6 (b), NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>C</sup> have CO<sub>2</sub> conversions of 66% and 50%, and CH<sub>4</sub> conversions of 67% and 58%, respectively. For NiCe@SiO<sub>2</sub><sup>A</sup>, these conversions correspond to the H<sub>2</sub> and CO yields of 68% and 64% with a H<sub>2</sub>/CO ratio of 1.8 (Fig. S6). The conventional NiCe/SiO<sub>2</sub><sup>Imp</sup> starts with similar conversion as the multi-yolk-shell nanotube catalysts, however, the conversions plummet after about 1 h (Fig. 6 (b)). The fast deactivation of NiCe/SiO<sub>2</sub><sup>Imp</sup> can be attributed to severe carbon formation, which has blocked the catalyst bed. The higher resistance to carbon deposition for the multi-yolk-shell catalyst than impregnated catalyst might come from the strong metal-support



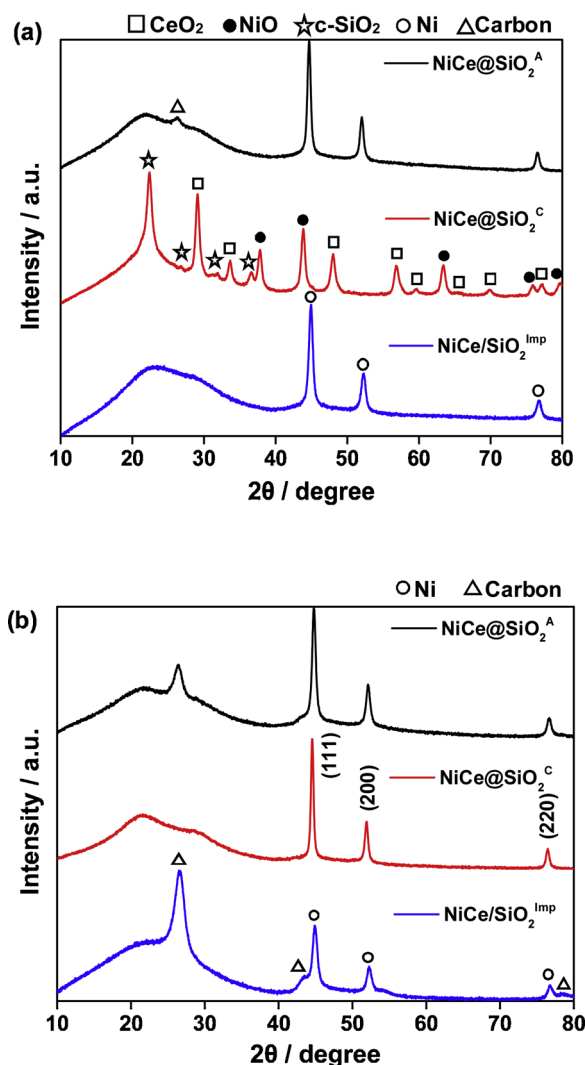


Fig. 7. XRD patterns for spent catalysts of  $\text{NiCe@SiO}_2^A$ ,  $\text{NiCe@SiO}_2^C$ , and  $\text{NiCe/SiO}_2^{\text{Imp}}$  after the TRM reaction in O/M ratios of (a) 1.1 and (b) 1.0 feed stream at 750 °C.

interaction due to confinement effect [66]. Both lower conversion and yield measured under reducing condition (O/M = 1.0) than oxidizing condition (O/M = 1.1) can be explained by the side reactions (reactions (8–10) and (12)) which facilitate carbon deposition [67]. Most of the carbon can be deposited on the catalyst by methane cracking reaction (8) at 750 °C, leading to the increase in  $\text{H}_2/\text{CO}$  ratio [55].

### 3.3. Characterization of the spent catalysts

Fig. 7 (a) and (b) show the XRD spectra of the spent catalysts after TRM at the O/M feed ratio of 1.1 and 1.0, respectively. The XRD measurements performed on the spent catalysts after the TRM at the O/M feed ratio of 1.1 indicate that the reduced metallic Ni ( $2\theta = 44.7^\circ$ ,  $52.0^\circ$ , and  $76.6^\circ$ ) and amorphous  $\text{SiO}_2$  shell maintained its phase in the  $\text{NiCe@SiO}_2^A$  and  $\text{NiCe/SiO}_2^{\text{Imp}}$  catalysts (Fig. 7 (a)). No  $\text{CeO}_2$  peaks are observed on  $\text{NiCe@SiO}_2^A$  and  $\text{NiCe/SiO}_2^{\text{Imp}}$  after the reaction because crystalline  $\text{CeO}_2$  phase turned into the amorphous phase in the presence of  $\text{H}_2$  at temperatures above 600 °C [59,68,69]. Despite the change of Ni and Ce phases during the reaction, the TEM image of the spent  $\text{NiCe@SiO}_2^A$  shows that the morphology of the multi-yolk-shell nanotube is preserved without collapsing, as shown in Fig. 8 (a). Further testing of  $\text{NiCe@SiO}_2^A$  at a higher O/M feed ratio of 1.25 also shows that higher oxidizer concentration in the feed stream does not influence the  $\text{NiCe@}$

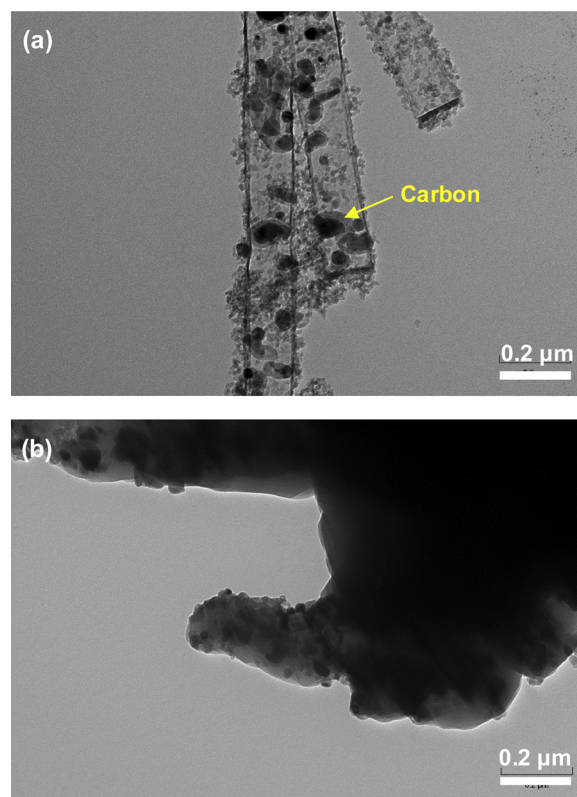


Fig. 8. TEM images of spent (a)  $\text{NiCe@SiO}_2^A$  and (b)  $\text{NiCe@SiO}_2^C$  after 20 h of TRM in O/M ratio of 1.1 feed stream.

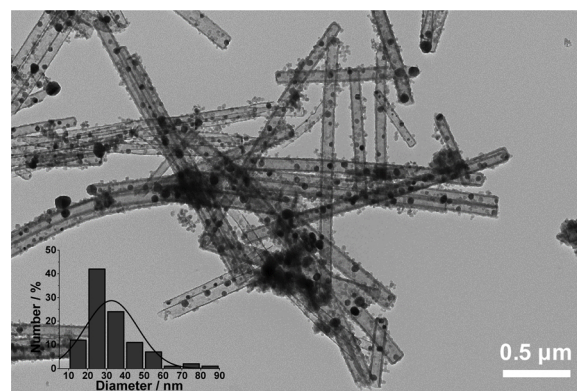


Fig. 9. TEM image of spent  $\text{NiCe@SiO}_2^A$  after 20 h of TRM in O/M ratio of 1.25 feed stream. Inset graph shows yolk size distribution.

$\text{SiO}_2^A$  catalyst morphology (Fig. 9). The mean yolk size of the spent catalyst (32.7 nm) is similar to the size of the fresh catalyst (32.9 nm). These results show that yolks are not likely to sinter during the reaction due to the strong interaction between the metal yolk and the silica shell [70,71]. However, in the case of  $\text{NiCe@SiO}_2^C$ , crystalline phases of NiO,  $\text{CeO}_2$  and  $\text{SiO}_2$  are observed for the spent catalyst due to re-oxidation at O/M ratio of 1.1 during the TRM (Fig. 7 (a)). The deactivation of  $\text{NiCe@SiO}_2^C$  is likely caused by oxidation of the active metallic Ni, followed by destruction of the multi-yolk-shell nanotube structure (Fig. 8 (b)). Fig. S8 shows the diffraction pattern of  $\text{NiCe@SiO}_2^C$  analyzed during the deactivation process. Both metallic Ni and  $\text{Ni}^{2+}$  phases are detected after 3 h of TRM, indicating that fully reduced Ni phase starts to be oxidized to the NiO phase at high O/M feed ratio, leading to the deactivation of the catalyst. It is important to note that a high amount of oxidizing species in the feed stream can still lead to the formation of carbon on the  $\text{NiCe@SiO}_2^A$  catalyst. As shown in the

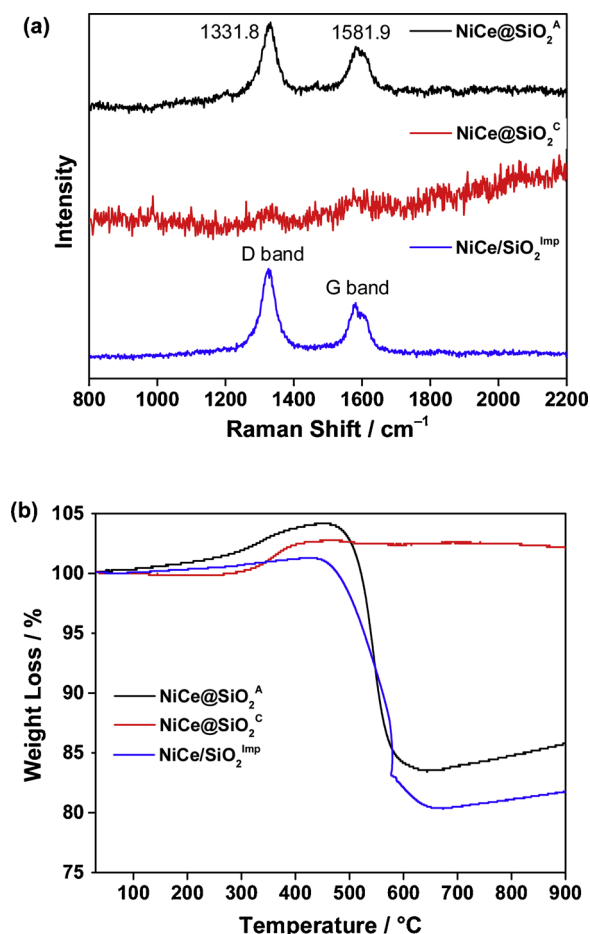


Fig. 10. (a) Raman spectra and (b) TGA profiles for spent catalysts of NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup> after the TRM reaction in O/M ratio of 1.0 feed stream.

diffraction pattern of the spent NiCe@SiO<sub>2</sub><sup>A</sup> (Fig. 7 (a)), carbon is detected at a two-theta of 26.6° [17,18]. The carbon deposition can also be observed in the TEM image of the spent catalyst (Fig. 8 (a)). Our results suggest that carbon deposition on the spent NiCe@SiO<sub>2</sub><sup>A</sup> is not high enough to affect the stability of the catalyst.

The XRD spectra of the spent catalysts after TRM at the O/M feed ratio of 1.0 show that all three catalysts have metallic Ni peaks along with wide amorphous SiO<sub>2</sub> peak, as shown in Fig. 7 (b). Similarly, CeO<sub>2</sub> turns to the amorphous phase and its diffraction peaks are not observed on all three spent catalysts after the reaction. The spent NiCe/SiO<sub>2</sub><sup>Imp</sup> catalyst has much stronger intensity for carbon peak at 26.6° than NiCe@SiO<sub>2</sub><sup>A</sup>, while no carbon peak is detected for NiCe@SiO<sub>2</sub><sup>C</sup> after 20 h of the TRM reaction. These results suggest that the multi-yolk-shell nanotube catalyst with smaller yolks presents high resistance to carbon deposition providing longer stability for TRM at the O/M feed ratio of 1.0. Raman spectra of the spent NiCe@SiO<sub>2</sub><sup>A</sup>, NiCe@SiO<sub>2</sub><sup>C</sup>, and NiCe/SiO<sub>2</sub><sup>Imp</sup> catalysts after the reaction at O/M feed ratio of 1.0 were collected to determine the nature of carbon formed on the spent catalyst. As shown in Fig. 10 (a), both the spent NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe/SiO<sub>2</sub><sup>Imp</sup> catalysts have carbon formations, in agreement with the XRD measurement, while carbon peaks are barely seen for NiCe@SiO<sub>2</sub><sup>C</sup> after 20 h of TRM. The two bands observed at 1331.8 cm<sup>-1</sup> and 1581.9 cm<sup>-1</sup> on the spent NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe/SiO<sub>2</sub><sup>Imp</sup> catalysts can be ascribed to carbon sp<sup>2</sup> bonds in which the first peak is assigned to the D band with defects or amorphous carbon, while the second peak belongs to the G band with ordered graphite structure [46]. TGA was performed to quantify the amount of carbon deposited on the spent catalysts after the reaction. As shown in Fig. 10 (b), the weight of the spent

multi-yolk-shell nanotube catalysts slightly increases starting from 260 °C due to oxidation of the catalyst. The sample weight loss occurs at temperatures between 450 °C and 650 °C for NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>Imp</sup> due to the gasification of the carbon formed during the TRM reaction. The deposited carbon amount is calculated to be 0.16 mg g<sub>cat</sub><sup>-1</sup> and 0.20 mg g<sub>cat</sub><sup>-1</sup> for NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe/SiO<sub>2</sub><sup>Imp</sup>, respectively. In consistent with the XRD and Raman analysis, the weight of NiCe@SiO<sub>2</sub><sup>C</sup> remains constant at temperatures between 450 °C and 900 °C, indicating that carbon species are not likely to form on the catalyst during 20 h of TRM. The high resistance to carbon deposition of NiCe@SiO<sub>2</sub><sup>C</sup> multi-yolk-shell nanotube catalysts can be possibly due to the strong binding of active Ni species to SiO<sub>2</sub>, as illustrated in the H<sub>2</sub>-TPR data. It is also possible that the unique morphology of the multi-yolk-shell nanotube structures does not allow carbon to be deposited on the active sites due to the confinement effect. Despite the unique morphology of the multi-yolk-shell nanotube catalysts, the XRD, Raman, and TGA results confirm that carbon can still form on larger yolks (NiCe@SiO<sub>2</sub><sup>A</sup>), while smaller yolks (NiCe@SiO<sub>2</sub><sup>C</sup>) exhibit higher resistance to carbon deposition at the O/M ratio of 1.0 feed stream.

#### 3.4. Effect of yolk size under reducing conditions

To understand the effect of yolk size on TRM activity, NiCe@SiO<sub>2</sub><sup>B</sup> with a mean yolk size between NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>C</sup> was synthesized and three multi-yolk-shell nanotube catalysts were evaluated at much higher methane concentration with an O/M feed ratio of 0.85. As shown in Fig. 11, NiCe@SiO<sub>2</sub><sup>C</sup> with a mean yolk size of 20.0 nm still presents a stable activity with CO<sub>2</sub> and CH<sub>4</sub> conversions of 73% and 61%, respectively. However, the NiCe@SiO<sub>2</sub><sup>A</sup> catalyst with the largest yolks deactivates within 2 h by carbon formation. NiCe@SiO<sub>2</sub><sup>B</sup> with a mean yolk size of 23.7 nm shows slightly longer stability than NiCe@SiO<sub>2</sub><sup>A</sup>, but the catalyst also loses its activity in 4 h due to the blockage of the catalyst bed by carbon formation. As shown in Fig. S9, carbon peaks in XRD are detected for both of the spent NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>C</sup> catalysts, but NiCe@SiO<sub>2</sub><sup>A</sup> with larger yolks have stronger carbon peak intensity than NiCe@SiO<sub>2</sub><sup>C</sup> with smaller yolks after the reaction with the O/M feed ratio of 0.85. Throughout the three multi-yolk-shell nanotube catalysts tested, NiCe@SiO<sub>2</sub><sup>C</sup> exhibits the most stable activity at both O/M ratio of 1.0 and 0.85 due to the fast carbon removal reaction, whereas the other catalysts with mean yolk size larger than 20.0 nm (NiCe@SiO<sub>2</sub><sup>A</sup> and NiCe@SiO<sub>2</sub><sup>B</sup>) deactivate at high CH<sub>4</sub> concentration feed streams.

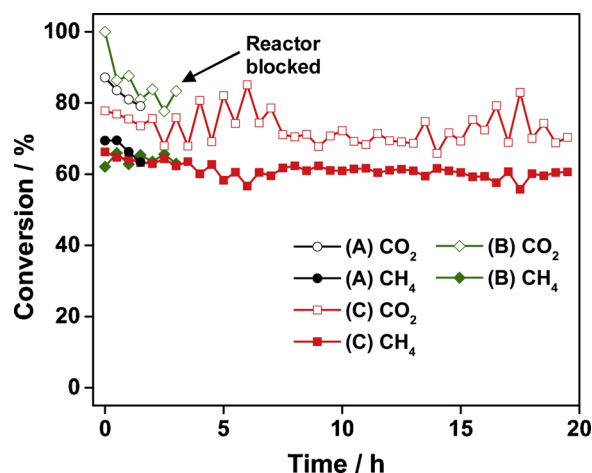
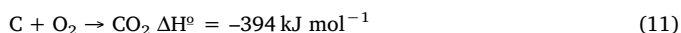
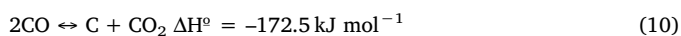
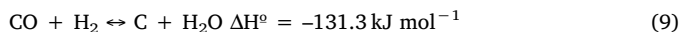
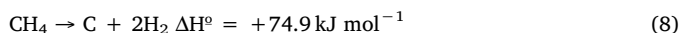


Fig. 11. CO<sub>2</sub> and CH<sub>4</sub> conversions of (A) NiCe@SiO<sub>2</sub><sup>A</sup>, (B) NiCe@SiO<sub>2</sub><sup>B</sup>, and (C) NiCe@SiO<sub>2</sub><sup>C</sup> at 750 °C in O/M ratio of 0.85 feed stream. Under this condition, the thermodynamic equilibrium conversions of CO<sub>2</sub> and CH<sub>4</sub> are 89.0% and 83.0%, respectively.



During the TRM reaction, carbon formation can occur via the following reactions: methane cracking (8), reduction of CO (9), and the Boudouard reaction (10). At the same time, the deposited carbon can be removed by the reverse reactions of (9) and (10), and the forward reaction of (11), in which carbon reacts with  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{O}_2$ , respectively. While these reactions occur simultaneously on the catalyst, carbon formation and removal reaction rates can be influenced by the Ni particle size. Different Ni particle sizes ranging in between 6 nm and 26 nm have been reported for the net formation of carbon on Ni-based catalyst [72–74]. It has been shown that the removal rate of carbon is faster than the formation rate of carbon on catalysts containing smaller Ni particles, indicating that large Ni particles are more susceptible to carbon formation [73,75]. In particular, the carbon formation rate in SRM is found to be directly related to the Ni particle size with smaller Ni particles resulting in a lower coking rate due to the low driving force for carbon diffusion through the Ni [76]. In addition to the carbon formation rates, smaller Ni particles are shown to yield carbon filaments with smaller diameters in DRM compared to filaments formed on larger Ni particles [77]. Growth of smaller diameter carbon filaments is not thermodynamically favorable, resulting in less carbon deposition compared to larger diameter carbon filaments. Carbon filament growth can be related to the equilibrium Gibbs free energy growth of graphite. Deviations from graphite's equilibrium Gibbs free energy are inversely proportional to particle diameter. The deviations from the graphite equilibrium value represent extra energy needed by the system to form filamentous carbon, therefore smaller Ni particles lead to larger deviations resulting in less carbon filament growth [78]. In POM, smaller Ni particles result in the formation of more hydrogen containing carbon species than graphitic or nanotube structure carbon [79]. Carbon species containing hydrogen are easily gasified and therefore do not cause catalyst deactivation, meaning that smaller particles are not as easily deactivated by carbon as larger particles. It stands to reason that the catalyst containing smaller yolks might form less and more easily removable carbon than the catalyst containing larger yolks. However, no distinctive conclusion can be made in terms of what Ni particle size is more beneficial to prevent carbon formation, as it highly depends on the chemistry and morphology of the catalyst. In addition to the Ni yolk size, Ni–Ce interaction can play a major role on the stability of the catalyst. Under reducing conditions i.e., O/M feed ratios of 0.85 and 1.0,  $\text{NiCe@SiO}_2^{\text{C}}$  has high resistance to carbon deposition possibly due to the high amount of  $\text{Ce}^{4+}$  concentration. The first step in methane reforming reactions is believed to start with  $\text{CH}_4$  dissociation to generate hydrocarbon species and carbon atoms [80]. Carbon atoms can be oxidized by reacting with  $\text{CO}_2$  (reaction (10)) and  $\text{Ce}^{4+}$  (reaction (12)). The reverse reaction of (12) could be observed for the  $\text{NiCe@SiO}_2^{\text{A}}$  and  $\text{NiCe/SiO}_2^{\text{Imp}}$  catalysts as they have high  $\text{Ce}^{3+}$  concentration, thereby can produce more carbon deposits compared to  $\text{NiCe@SiO}_2^{\text{C}}$  [80].

### 3.5. Effect of yolk size under oxidizing conditions

The active metallic Ni phase in small yolks can be re-oxidized by adsorbing oxygen species from the feed gases or interaction with  $\text{CeO}_2$  at O/M feed ratios higher than 1.0. Large Ni yolks can have slower carbon removal rate leading to carbon deposition even at higher O/M ratios feed stream, as shown in Fig. 7 (a) and Fig. 8 (a). However, it has been hypothesized that the carbon formation on large Ni particles can

prevent Ni metal from being oxidized in the high oxygen-containing feed stream (O/M ratio > 1.0) [81]. On the other hand, carbon formation rate is slower than the carbon oxidation rate on the small yolks ( $\text{NiCe@SiO}_2^{\text{C}}$ ), therefore, the amount of deposited carbon may not be sufficient enough to prevent the oxidation of metallic Ni to NiO, leading to deactivation of the catalyst. In contrast to the  $\text{NiCe@SiO}_2$  multi-yolk-shell nanotube catalyst, the conventional  $\text{NiCe/SiO}_2^{\text{Imp}}$  catalyst exhibits stable activity without both Ni oxidation and carbon formation confirmed by XRD at the O/M feed ratio of 1.1 (Fig. 7 (a)). This can be explained by the fact that  $\text{NiCe/SiO}_2^{\text{Imp}}$  has stronger interaction between dispersed Ni and Ce species confirmed by  $\text{H}_2$ -TPR and XPS. The  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox property on  $\text{CeO}_2$  provides high surface and bulk oxygen vacancies [29]. Therefore, it is possible that the oxygen species migrate to the oxygen vacancies on  $\text{CeO}_2$ , which hinders Ni species from being oxidized. The stable activity of  $\text{NiCe@SiO}_2^{\text{A}}$  and  $\text{NiCe/SiO}_2^{\text{Imp}}$  at O/M ratio of 1.1 can also be explained by Ce effect as aggregated Ni yolks and dispersed Ni particles in interaction with Ce lead to the formation of more  $\text{Ce}^{3+}$  species evidenced by  $\text{H}_2$ -TPR and XPS. Availability of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  species can shift the equilibrium of the reaction (13) and facilitate Ni oxidation [80]. Both  $\text{NiCe@SiO}_2^{\text{A}}$  and  $\text{NiCe/SiO}_2^{\text{Imp}}$  have higher  $\text{Ce}^{3+}$  concentration compared to  $\text{NiCe@SiO}_2^{\text{C}}$  and show stable activity without Ni oxidation. On the contrary, the forward reaction of (13) can be observed for the  $\text{NiCe@SiO}_2^{\text{C}}$  as it has high  $\text{Ce}^{4+}$  concentration, thereby can oxidize active Ni yolks.

In summary, our results indicate that carbon formation and removal rates need to be balanced to obtain stable performance under the TRM by controlling the Ni yolk size and Ni–Ce interaction. If the carbon formation is faster than carbon removal process, the carbon will deposit onto the catalyst, whereas if the carbon removal reaction rate is faster than carbon formation rate, the metallic Ni species can be oxidized to NiO by exposing to oxygen species, which both cases can deactivate the catalyst [82,83]. While the effect of yolk size and Ce effect on the TRM activity can be pronounced, other structural parameters, such as shell thickness and tube diameter of the multi-yolk-shell nanotube catalysts, should be systematically analyzed in future studies.

## 4. Conclusions

Different morphologies of  $\text{NiCe@SiO}_2$  multi-yolk-shell nanotube catalysts were synthesized by controlling the water to surfactant ratio in the reverse microemulsion method. The multi-yolk-shell nanotube catalyst prepared at a high water/surfactant ratio forms smaller yolks surrounded by a longer diameter silica tube shell, whereas a low water/surfactant ratio produces larger yolks with a shorter diameter tube shell. Catalysts prepared with small and large yolks show distinct characteristic behavior at various feed gas ratios under TRM. At a low O/M feed ratio, the  $\text{NiCe@SiO}_2$  multi-yolk-shell nanotube catalysts exhibit high resistance to carbon deposition due to its confinement effect. In contrast, the conventional  $\text{NiCe/SiO}_2^{\text{Imp}}$  catalyst produces a high amount of carbon deposition on the catalyst, which deactivates the catalyst fast. The  $\text{NiCe@SiO}_2$  multi-yolk-shell nanotube catalyst with smaller yolks forms less carbon compared to the catalyst with larger yolk sizes (> 20 nm) possibly due to the facile oxidation of carbon on the smaller Ni yolks and low  $\text{Ce}^{3+}$  concentration. On the other hand, at a high O/M feed ratio, the  $\text{NiCe@SiO}_2$  catalyst containing smaller yolks tends to be easily re-oxidized by oxygen species leading to the catalyst deactivation followed by destruction of multi-yolk-shell nanotube morphology. However, the  $\text{NiCe@SiO}_2$  with larger yolks shows stable activity without oxidation possibly due to the slower carbon removal reaction rate and high  $\text{Ce}^{3+}$  concentration. Our results show that the morphology of the  $\text{NiCe@SiO}_2$  multi-yolk-shell nanotube catalysts will influence the TRM activity at different O/M feed ratios, and this tunable morphology can be engineered for obtaining high TRM activity and stability.



## Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.118037>.

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